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SOME GASEOUS REACTIONS UNDER THE INFLUENCE OF IONIZING AGENTS

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BY

BARNARD MITCHELL MARKS

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IS HYDROGEN PEROXIDE FORMED IN ELECTROLYTIC GAS BY ALPHA RAYS?

BY BARNARD M. MARKS

The combination of hydrogen and oxygen at ordinary temperature has been produced in a variety of ways. The two modes of activation of immediate interest to the following experiments are activation by resonated mercury atoms and ionization by alpha particles from radon.

The first mode of activation has recently been used by Marshall[1] and by Bates and Taylor[2] who reported the formation of hydrogen peroxide by the use of resonated mercury atoms in mixtures of hydrogen and oxygen. They determined the amount of peroxide in their product by titration with permanganate. The hydrogen peroxide, as well as the water formed in the reaction, were removed together by condensation in a trap surrounded by a carbon dioxide-ether bath. They found that the amount of hydrogen peroxide produced was a function of the rate of flow as well as the ratio of oxygen to hydrogen.

The second method of activation was used in 1914 by O. Scheuer[3] who reported some extensive experiments on the interaction of hydrogen and oxygen under the influence of alpha-radiation from radon. He used the Lind[4] alpha-ray bulb as well as the system of Cameron and Ramsay[5]. The amount of reaction was determined by the change in pressure only. In order to account for the excess of hydrogen that he obtained on analysis of the initial and final systems over that required for the simple formation of water, he postulated the formation of hydrogen peroxide. In his conclusion he states: ". . . the analysis shows moreover the absence of ozone, or, since ozone cannot exist in the presence of hydrogen peroxide and mercury (as is the case in our experiments) . . ." This statement shows that in the system that he used there was mercury present. This will account for the disappearance of oxygen in excess of the proper quantity required for the formation of water.

Scheuer's experiments were carried out in a static system with no direct analysis for hydrogen peroxide; all of the excess of hydrogen in the residual gases being attributed to the formation of hydrogen peroxide. *It is evidently important to carry out the experiment under conditions where a direct analysis for hydrogen peroxide can be made.* In the present work such experiments were made in a flow system using alpha-particle ionization as shown in Fig. 1. The products of the reaction were collected in a liquid-air trap for a period of

[1] A. L. Marshall: J. Phys. Chem., 30, 34 (1926); J. Am. Chem. Soc., 49, 2446 (1927).

[2] J. R. Bates and H. S. Taylor: J. Am. Chem. Soc., 49, 2763 (1927).

[3] O. Scheuer: Compt. rend., 159, 423 (1924).

[4] S. C. Lind: "Chemical Effects of Alpha-Particles and Electrons," 86 (1928).

[5] A. T. Cameron and Wm. Ramsay: J. Chem. Soc., 91, 931, 1266, 1593 (1907); 92, 966, 992 (1908).

72 hours so as to obtain a measurable concentration. The products were then allowed to distil into another liquid-air trap constructed so that it could be removed and weighed. During the distillation and the time required for the trap to warm sufficiently to remove it from the collection system, the exit gases were allowed to bubble through a solution of potassium iodide. If ozone is produced in the reaction its concentration must have been less than the vapor pressure of ozone at liquid air temperature as the above test gave no

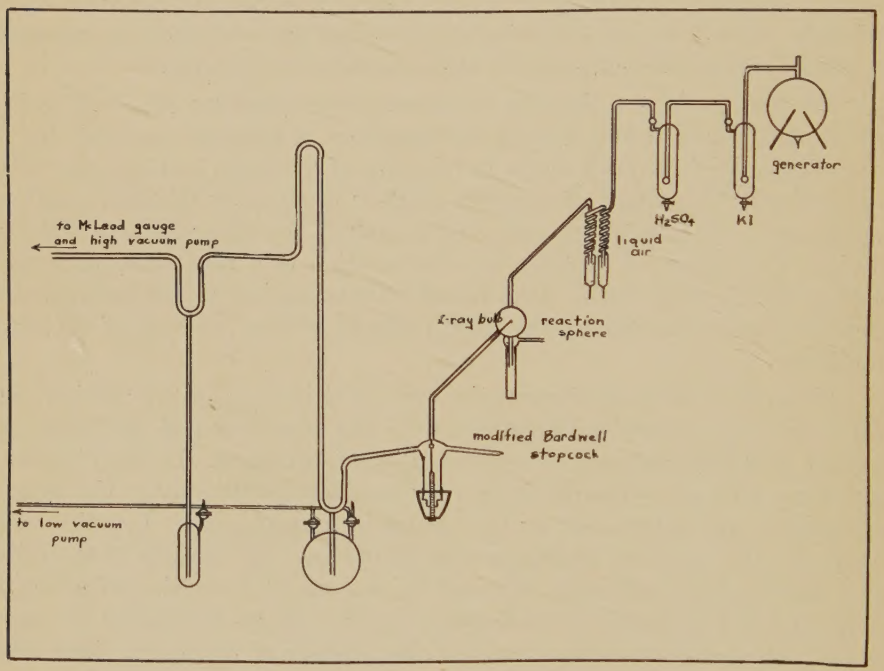

FIG. 1

evidence of the presence of ozone. The receiver was stoppered immediately after it was removed from the collection system with a fitted stopper containing a plug of P_2O_5 to prevent loss of moisture. The whole was allowed to warm to room temperature and then weighed. Immediately after weighing, the receiver was added to an acid solution of the proper concentration for permanganate titration. The blank and sample were found to require the same amount.

In a second experiment the receiver was constructed so that it was immediately below the reaction chamber. This eliminated any possibility of loss due to the catalytic decomposition of the hydrogen peroxide due to the walls of the reaction vessel. A run of 92 hours was made during which time the receiver was immersed in liquid air. After that time, the receiver was warmed sufficiently to remove it and then placed in a desiccator as before. Immediately after weighing the contents of the receiver, the amount of per-

oxide was determined by adding a drop of 0.038 N permanganate solution. It was found that the amount of peroxide formed during that period was insufficient to affect the color. In an experiment to determine the sensitivity of the method used, it was found that 1.5×10^{-7} equivalents was sufficient to decolorize that amount of permanganate immediately.

In these experiments it was found that the amount of water collected in the traps was greater than the amount that would be predicted from the decrease of pressure in static experiments. This excess water was probably due to the liberation of occluded water from the walls of the reaction system. The results of the above experiments clearly indicate that the amount of peroxide formed in electrolytic gas by alpha rays, if any at all is formed, is very very small and the previously reported results obtained in a static system are in error probably due to the presence of mercury, which combined with part of the oxygen, leaving an excess of hydrogen, which was not evidence, however, of the formation of hydrogen peroxide.

Summary

No evidence of the formation of hydrogen peroxide by the action of alpha-particles on electrolytic gas has been obtained in experiments where a direct test was made for it.

The absence of ozone was also shown by direct test.

An explanation of the results of previous investigations, where the presence of hydrogen peroxide was claimed, is given.

The author wishes to express his appreciation to Dr. S. C. Lind who suggested the problem and under whom the work was carried out, and to Drs. R. S. Livingston and G. Glockler for their assistance.

University of Minnesota,
Minneapolis.

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VI. THE ACTION OF ELECTRICAL DISCHARGE ON GASEOUS HYDROCARBONS.[1]

The effect of high-speed cathode rays on paraffin hydrocarbons.

By S. C. Lind,[2] B. M. Marks[3] and G. Glockler.[4]

Abstract.

It has been found that the hydrocarbons methane, ethane, propane, and butane are decomposed by the high-speed electrons (125,000 volts) which are emitted through the thin glass window of a Slack-Lenard-Cathode Ray-Tube. Hydrogen is one of the products of decomposition. An estimate is made of the number of molecules reacting per electron crossing the reaction tube and of the number of ion pairs produced in the reacting gas per electron traversing it. The comparison of these ratios shows that the number of molecules reacting and the number of ion pairs formed are of the same order of magnitude.

In former papers[5] it has been shown that the gaseous hydrocarbons can be activated by ionizing agents such as alpha rays from radon or the electrical discharge as obtained in an ozonizer. It is to be expected that other forms of electrical discharge would produce similar chemical action in the hydrocarbon gases. The recent development of the Slack type of high-speed cathode ray tubes[6] has made it possible to study the chemical reactions produced by electrons of high velocity. The arrangement is similar to the system in use with radon[7] where the activating agent is separated in an "alpha ray bulb" of very thin glass walls (transparent to alpha particles) from the chamber containing the reacting

[1] Condensed from part III of a thesis submitted by Barnard M. Marks to the Faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, October, 1929. Manuscript received January 19, 1931.

[2] Director of the School of Chemistry, University of Minnesota.

[3] Chemist, Du Pont Viscoloid Company, Arlington, New Jersey.

[4] Associate Professor of Chemistry, University of Minnesota.

[5] S. C. Lind and D. C. Bardwell, J. Am. Chem. Soc., **48**, 2335-2351 (1926), and S. C. Lind and George Glockler, J. Am. Chem. Soc., **52**, 4450-60 (1930).

[6] M. C. Slack, J. Am. Optical Soc., **18**, 123-126 (1929)

[7] S. C. Lind, "The Chemical Effects of Alpha Rays and Electrons," 2d Ed., p. 86 (1928). Chem. Cat. Co., N. Y.

* Headquarters, Columbia University, New York City. Printed in U. S. A.

gases. In the cathode ray tube the hot filament, which is the source of electrons, is separated from the reaction chamber proper by a thin glass window which is transparent to electrons. Any reaction produced must then be due to the activating influence of high-speed electrons. Methane, ethane, propane and butane have been studied and it has been found that these gases undergo reaction under the influence of high-speed electrons, as was to be expected. The progress of the reaction was followed by the amounts of hydrogen liberated. The authors are grateful to the Westinghouse Lamp Works, Bloomfield, New Jersey, for the Lenard ray tubes used in these experiments.

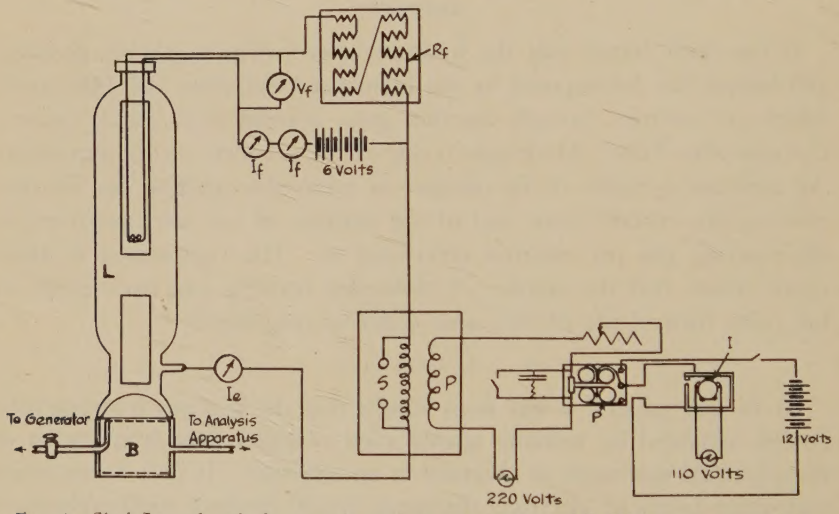

FIG. 1. Slack-Lenard cathode ray tube and electrical setup: S-P High-tension transformer. Rf, Vf, If, = filament circuit. I, P = interrupter and contact for primary transformers circuit. B = reaction bulb. L = Lenard tube.

APPARATUS.

The arrangement of the all glass apparatus is shown in Figure 1. The electrical set-up consisted of an X-ray outfit operated by a special timing device giving the intermittent voltage recommended for these Lenard tubes. The timing, one second "on" followed by five seconds "off," was secured by means of a cam attached to the shaft of a constant-speed motor. The cam operated the special relay that interrupted the primary circuit of the transformer. This relay, in addition to having large contact areas, was constructed with an electromagnetic "make and break." The rapidity of its action together with the condenser and resistance that were connected across the contacts reduced arcing to a

minimum and the necessity of readjusting the timing mechanism was almost entirely eliminated. The voltage was regulated by means of a sphere gap. The spheres were of one centimeter diameter and were approximately 19.2 cm. apart.[8]

The reaction cell is shown in Fig. 2. The windows of the cell were made of thin aluminum foil 0.01 mm. thickness.[9]

The use of such thin windows makes it necessary to support them by means of a wire grid. The grid did not reduce the electron stream appreciably as its wires covered but a negligible area.

MATERIALS USED.

The hydrocarbons used in these experiments were prepared by the reaction of the proper Grignard reagent with water. The gaseous

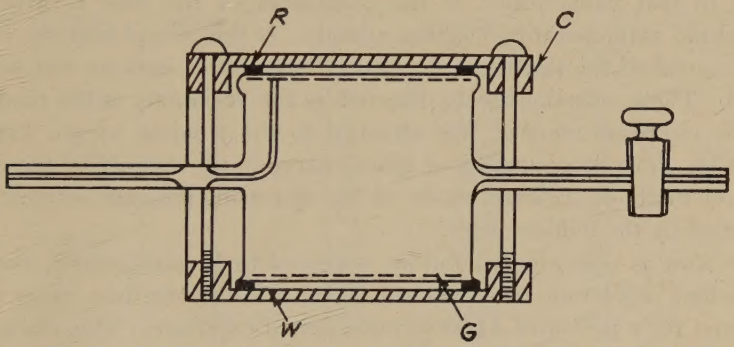

FIG. 2. Reaction bulb detail: G = grid. W = Al-window. R = washer. C = clamp.

hydrocarbons, which were generated as needed, were led through traps of concentrated sulfuric acid. Several traps were placed in series so as to remove any ether and unsaturated hydrocarbons that might be present in the gas stream. The gases next passed through a column of tightly packed glass wool to remove any sulfuric acid spray that might be carried over in the gas stream. The purified gases then passed into the reaction cell.

EXPERIMENTAL PROCEDURE.

Before any actual experiments were carried out a calibration of the Lenard ray tube was made. This consisted in varying the filament current until the amount of darkening of a "fast" blueprint paper, in

[8] Fowle, F. L., Smithsonian Physical Tables, 7th Ed., p. 254 (1923).

[9] We wish to thank Professor Farrington Daniels for these foils. They were furnished by the Aluminum Company of America and were similar to the ones used to protect his Coolidge tube from the corrosive action of some of his reaction systems. Busse, W. F., and Daniels, F. J., Am. Chem. Soc., **50**, 3271 (1928).

a definite time interval, matched the sample supplied by the Westinghouse company. This was taken as the maximum safe electron emission of the tube.

The method of experimentation was standardized as follows: The reaction cell was flushed out overnight, so that initially the reaction cell was filled with a sample of pure gas. Just before starting the experiment a portion of the gas in the cell was removed for analysis and an additional quantity of gas admitted to adjust the pressure to the desired value (usually atmospheric pressure). The voltage on the tube was then increased slowly so that "hardening" of the tube was accomplished and the danger of destroying the thin glass window was minimized. As soon as the operating voltage (125-130 kilovolts) was reached the filament current was turned on. It was increased in small steps to that value found in the calibration of the tube to give the maximum safe operating electron stream. It was found that the absolute control of the intensity of radiation was not as easy as was anticipated. These variations were detected by the variations in the readings of the milliammeter that was attached to the window of the Lenard ray tube. The accumulation of space charge in the vicinity of the reaction cell might be the explanation of the decreasing amounts of electrons recorded by the milliammeter.

As soon as operating conditions appeared to be satisfactory, the intermittent regulation was switched in and the hydrocarbon gases were radiated for a period of 3,600 seconds' actual exposure. This made the operating time approximately 6 hours. Readings were taken every 10 minutes during the experiment, so that calculations are based on an average of these readings. The milliammeter readings gave the total amount of current passing through the tube, but not an actual measure of the external electron stream.

In order to provide as nearly a constant source of current as possible the filament of the cathode ray tube was heated by two storage batteries that were connected in parallel. These were charged after each run so as to provide further assurance of the constancy of the heating current. As it was necessary to increase the filament current while the high potential was applied, a number of single-pole, single-throw switches were connected in parallel with small resistances made of chromel wire. These small resistances were in series with the filament of the Lenard ray tube and by shunting them out the current could be increased in small steps. Unless the current that heated the filament was increased in small steps there was a danger of breaking the thin

glass windows of the cathode ray tube by the sudden rush of a large number of electrons. As these electrons pass through the window they necessarily give up some of their energy to the window. This energy from such a large number of electrons might be sufficient to heat the window to its softening temperature and consequently cause its failure. The single-pole, single-throw switches were operated by means of a long glass tube, so that there was no necessity of approaching dangerously near to the high potential system.

Because the loss of energy of electrons in passing through the window of the tube varies inversely with the square of the accelerating

TABLE I.

Determination of Hydrogen in the Resulting Gases.

Expt. No.	Hydro-Carbon	Method of Analysis	Hydrogen found (vol. %)	t Time of run (seconds)	c Current (milli-amp.)	Molecules H_2 / Electron (average)
1	CH_4	I	.66	1,560	0.16	7.0
18		I	2.76	3,600	.26	
3	C_2H_6	I	1.73	3,600	.14	11.6
5		II	6.46	3,600	.26	
7		II	2.27	3,120	.24	
6		I	4.82	3,600	.22	
8	C_3H_8	II	1.83	3,600	.22	9.3
9		I	3.82	3,600	.19	
10		I	1.18	805	.17	
11		II	1.57	3,600	.23	
12		I	2.47	3,600	.24	
13	C_4H_{10}	II	3.79	3,600	.21	11.6
14		I	6.14	3,600	.24	
17		II	3.15	3,600	.25	

voltage, the permitted electron current must be much smaller if the potential is low. To eliminate any difficulties from this source, the tube was always raised to its full operating voltage before lighting the filament.

ANALYSIS.

The *initial* gases as well as the *final* reaction products were analyzed for hydrogen under as near identical conditions as possible and the hydrogen reported is based on the difference of these two results. Two methods of analyzing the gases were used in these experiments.

In the first method (I) the gas resulting from an experiment was analyzed for hydrogen by diffusion through a palladium thimble in the usual way, without, however, attempting fractionation at low tempera-

tures. In the second method (II) the sample of gas obtained from an experiment was separated by means of liquid air into two fractions, one containing hydrogen and methane and the other the heavier gases of the mixture.

RESULTS.

The results obtained are given in Table I. The ratio of hydrogen formed per electron was calculated as follows:

$$\frac{M_{H_2}}{E} = \frac{\%H_2}{100} \times 60.6\text{ cc.} \times \frac{273^\circ\text{ C.}}{298^\circ\text{ C.}} \times \frac{96{,}500}{22{,}400} \times \frac{1}{\text{time}} \times \frac{1}{\text{amperes}}$$

The volume of the reaction vessel is 60.6 cc. Hydrogen was chosen as a measure of chemical reaction because it does not react further under electrical discharge.

DISCUSSION OF RESULTS.

The experimental results presented may be considered in the following way. Only a small fraction of the current indicated by the milliammeter will actually cross the reaction tube. Busse and Daniels[10] found that about one per cent of the energy of the cathode rays is expended in the reaction vessel. If it is then assumed that only one per cent of the electrons enter the reaction vessel, then on the average there are 1,000 molecules of hydrogen formed per electron. But for every hydrogen molecule formed two hydrocarbon molecules most likely react, so that about 2,000 molecules of hydrocarbon react per electron traversing the reaction chamber.

On the other hand, an estimate of the number of ion pairs formed by one electron may be obtained as follows: The equation of Thomson[11] concerning the loss of energy suffered by an electron when crossing material substances is

$$V_o^2 - V_x^2 = K \times \text{density} \times \text{distance traversed}$$

where V_o = the initial energy of the electron

V_x = the energy of the electron after having traveled the distance "x" in the material.

Using this equation and the mass absorption coefficient

$$K = 4.32 \times 10^{11}$$

for substances such as metals (Al, Cu, Au, Ni) and glass, the energy of 130,000 volt electrons after passing the glass window (0.0005 cm.

[10] J. Am. Chem. Soc., **50**, 3283 (1928).

[11] J. T. Thomson, "The Conductivity of Electricity through Gases," p. 378. Univ. Press, Cambridge, 1911.

thick) is 127,500 volts. The reaction vessel was at a distance of about 3 cm. from the glass window and the electrons suffered an energy loss in this air layer. If it is assumed that the mass absorption coefficient is the same for all substances then the loss of energy in the air layer can be calculated

$$(127{,}500)^2 - V_x^2 = 4.32 \times 10^{11} \times \frac{28}{22{,}400} \times 3.00 \text{ cm.}$$

and the energy of the electrons after crossing the air layer is $V_x = 121{,}000$ volts. These electrons now cross the aluminum foil of the reaction vessel and they enter the reaction gases with an energy of 116,000 volts.

The loss in the hydrocarbon gases can be estimated in the manner of the above calculations $(116{,}000)^2 - V_x^2 = 4.32 \times 10^{11} \times$ density x 3.5 cm. and in the case of propane amounts to about 14,000 volts. The ionization potential of propane must be 10-14 volts so that one electron can produce about 1,000 ion pairs. The comparison of the ratios "moles of hydrocarbon reacting per electron" and "number of ion pairs per electron" shows that about 2 molecules of hydrocarbon react per ion pair. Of course, it is realized that these calculations are merely rough estimates, but they point out which quantities must be measured more accurately to obtain quantitative results.

It is interesting to note that Busse and Daniels arrive at a similar conclusion in regard to the decomposition of oxygen into ozone by high-speed electrons, namely, that only a small number (of the order of unity) of molecules react per ion pair, showing that these reactions have apparently some analogy to the reactions produced by alpha particles.

One of the original objects of the present work was to investigate whether the relative amounts of chemical reaction produced by high-speed cathode rays in the four hydrocarbon gases investigated might be a measure of their relative stopping powers for swift cathode rays. The reasoning was as follows:

When alpha particles act on the same four hydrocarbons the amount of reaction per ion pair remains constant, but the amount of action per unit of path of the alpha particle which entirely traverses the gas is in proportion to their relative stopping powers or about as 1 : 1.8 : 2.5 : 3.2 for methane, ethane, propane and butane, respectively. If then sufficiently swift cathode rays could be obtained to

go entirely across the reaction cell in approximately straight lines, possibly relations similar to those for the alpha particles would be discovered. The experimental results in Table I do not indicate such a relation and it remains to be shown whether this finding is simply due to real lack of such proportionality or whether the experimental errors have been too great to discover it. The calculations on the energy of the cathode rays do not indicate lack of energy either before reaching or on passing across the reaction tube.

Minneapolis, Minn.

Written discussion, preferably typewritten and in triplicate, of this paper is invited and should be sent to The Electrochemical Society, Columbia University, New York City.

VITA

The author, Barnard Mitchell Marks, was born in Kansas City, Missouri on July 28, 1905. He graduated from the Kansas City (Mo.) High School in 1922. He received the degrees of B.S. 1926, and Chemical Engineer, 1927, from the University of Missouri. He entered the Graduate School of the University of Minnesota in September, 1927, and received the degree of Doctor of Philosophy in December, 1929. Major Physical Chemistry, minor Organic Chemistry. He held an Assistantship in the University of Missouri during 1926-27, and also a graduate Assistantship in the Department of Chemistry, University of Minnesota, during 1927-28 and 1928-29. He is now Research Chemist for the Du Pont Viscoloid Company, Arlington, N. J.

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